Design, synthesis and properties of new materials based on densely crosslinked polymers for polymer optical fiber and amplifier applications

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On the synthesis of densely crosslinked high T_g polycarbosiloxanes

An evaluation of new polysiloxane networks with norbornane groups.

ABSTRACT

New siloxane prepolymers derivatized with norbornane and with crosslinkable funtionalities have been synthesized successfully. Norbornane fragments have been introduced either into the polysiloxane backbone or onto silicon as a side group. The polymerization characteristics did not change compared to previously described polycarbosiloxanes. From these prepolymers, highly dense crosslinked networks were prepared. The introduction of norbornane structures resulted in an effective increase in T_g, which was the aim of the investigation. Introduction of norbornane as silicon side group led to the most effective increase in T_g after the crosslinking reaction was complete. A transparent glassy material has been obtained with a T_g of 115^{o}C, which is 85^{o}C higher than that of a comparable polymer with methyl side groups instead of norbornane.

INTRODUCTION

Densely crosslinked systems such as the polycarbosiloxanes, subject of this thesis, show a brittle mechanical behavior above the glass transition temperature.[1,2] Although application as a core material in a strong and tough thermoplastic tubing may result in mechanically stable polymer optical fibers, the sensitivity to crack formation, at temperatures immediately above the T_g, might lower the mechanical stability in the long term. With that, also the optical quality will deteriorate in the long run as the number of scattering centers will grow with the number of cracks. Below the glass transition temperature, the densely crosslinked systems are reasonably tough materials, however.[1,2] The polycarbosiloxane networks showed a tough-to-brittle transition around the glass transition temperature (with increasing temperature). To ensure long-term mechanical stability in high temperature applications, densely crosslinked systems should possess a glass transition temperature higher than or at least close to the application temperature. To reach high glass transition temperatures for polysiloxane-based systems, either an extremely high crosslink density or the introduction of bulky groups is necessary. A higher crosslink density will lead to a molecular structure close to that of quartz glass (SiO_2). As this introduces an even higher brittleness, it is not the right solution. Incorporation of bulky groups, either as side group or into the backbone, will result in materials with higher T_g's. To reach the aim of high-temperature mechanical reliability of polymer optical fibers prepared from densely crosslinked polycarbosiloxanes, we have synthesized new alkoxysilane monomers with norbornane groups. Norbornane is a very bulky, bicyclic molecule and is fully saturated. Introduction of norbornane will not lead to additional absorptions of light by electronic transitions, making it interesting for application in polymer optical fibers. Norbornanes with a single or a double unsaturation exist and are commercially available. These unsaturated norbornanes can undergo a versatile set of chemical reactions among which are hydrosilylation reactions.[3,4] Hydrosilylation is a powerful synthetic technique to produce all kinds of organofunctional chloro- and alkoxysilanes.[5] Based on the hydrosilylation reaction, difunctional alkoxysilane monomers were synthesized which

introduce norbornane either as a side group or in the backbone structure during the polymerization of polysiloxanes.

We have evaluated the influence on the T_g and on the mechanical, thermal and optical properties of the incorporation of these bulky norbornane groups in polycarbosiloxane networks.

EXPERIMENTAL

Materials:

Dimethylchlorosilane and the platinum-divinyltetramethyldisiloxane complex with 3-3.5 wt % of platinum in vinyl-terminated polydimethylsiloxane were purchased from ABCR and were used as received. Methyldichlorosilane, bicyclo[2.2.1]-2-heptene (norbornylene), 5-vinyl-2-norbornene, bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) and 2-mercaptobenzothiazole were used as received from Acros Organics. Diethyl ether was distilled from P_2O_5 and just before use from $LiAlH_4$. Pentane was distilled from P_2O_5. 1-Methyl-2-pyrrolidinone (NMP) was distilled from CaH_2 and stored above 4 Å molecular sieves. Ethanol (pro analysis) and pyridine (pro analysis) were used as received.

Methylnorbornanediethoxysilane (MNDES)

19.4 g (0.17 mol) of methyldichlorosilane and 15.9 g (0.17 mol) of norbornylene were combined in a 250 mL 3-neck round-bottomed flask with 15 ppm of platinum catalyst. The mixture was allowed to react for 24 h at room temperature under a nitrogen atmosphere. The raw product was used in the synthesis of methylnorbornanediethoxysilane without further purification.

A 250 mL 3-neck round-bottomed flask was equipped with an addition funnel, a cooler, a nitrogen inlet and a magnetic stirrer. The raw methylnorbornanedichlorosilane (the total yield of the above-described reaction) was dissolved in 50 mL of dry diethyl ether. To the solution, 18.4 g (0.40 mol) of ethanol diluted with 18 g of dry diethyl ether were added dropwise. After the addition of ethanol, pyridine was added to complete the reaction (followed by ^{1}H-NMR). The pyridine-HCl salts were subsequently removed by filtration. The diethyl ether was removed by rotation evaporation. Further purification of the obtained product was achieved by distillation using a spinning band distillation apparatus (plate number = 20), yielding 8.4 g (23%) of pure methylnorbornanediethoxysilane (T_b = 70^{o}C at p = 0.42 mbar).

^{1}H-NMR ($CDCl_3$); δ (ppm): 0.10 (s, Si-CH_3), 1.2 (dt, Si(O$CH_2\underline{CH_3}$)$_2$), 3.75 (dq, Si(O$\underline{CH_2}CH_3$)$_2$), 0.70 (t, Si-CH, norbornyl), 1.10 - 2.35 (m, C_6H_{10} - norbornyl).

^{29}Si-NMR ($CDCl_3$); δ (ppm): -6.9 (s).

Bis(dimethylethoxysilyl)ethylnorbornane (BENOR)

A 250 mL 3-neck round-bottomed flask, equipped with a nitrogen inlet and a magnetic stirrer, was charged with 24.0 g (0.20 mol) of vinylnorbornene and 37.8 (0.40 mol) of dimethylchlorosilane and 15 ppm of platinum catalyst. The mixture was heated to 50^{o}C for 4 days and was kept under an atmosphere of nitrogen. Hereafter the Pt-catalyst was killed by the addition of 2-mercaptobenzothiazole. The raw product was used without further purification.

The unpurified bis(dimethylchlorosilyl)ethylnorborane obtained from the above-described reaction was combined with 200 mL of dry pentane and 39.7 g (0.40 mol) of NMP in a 500 mL 3-neck round-bottomed flask equipped with an addition funnel, a nitrogen inlet, a magnetic stirrer and a cooler. 18.4 g (0.40 mol) of ethanol were added dropwise to the solution. The reaction mixture was heated to 40^{o}C halfway through the addition of ethanol. After the addition was complete the reaction mixture was allowed to stand for 1 h at 40^{o}C. Thereafter the mixture was cooled down to room temperature and filtered over a 0.20 μm Teflon membrane filter. The filtrate was put into a freezer for 1 night to allow the residual NMP-salts to crystallize after which the crystals were filtered off. The pentane was removed with a rotation evaporator. Further purification of the product was achieved by spinning band distillation, yielding 19.5 g (29%) of pure bis(dimethylethoxysilyl)ethylnorbornane (T_b = 93^{o}C, p = 0.3 mbar).

^{1}H-NMR ($CDCl_3$); δ (ppm): 0.02 (m, Si-CH_3), 1.12 (dt, Si(O$CH_2\underline{CH_3}$)$_2$), 3.60 (dq, Si(O$\underline{CH_2}CH_3$)$_2$), 0.50 (t, Si-CH_2, Si-CH, ethylnorbornane), 0.40 - 2.20 (m, C_8H_{12} - ethylnorbornane).

^{29}Si-NMR ($CDCl_3$); δ (ppm): 15.1 - 17.3 (m).

Bis(dimethylethoxysilyl)norbornane (BNOR)

A 250 mL 3-neck round-bottomed flask was charged with 20 g (0.22 mol) of norbornadiene and 41.2 g (0.44 mol) of dimethylchlorosilane and 15 ppm of platinum catalyst. The mixture was heated to 40^{o}C and allowed to react for 14 days under a nitrogen atmosphere. Throughout

the reaction, the conversion was followed by NMR. The product, bis(dimethylchlorosilyl)norbornane, was used without further purification.

A 500 mL 3-neck round-bottomed flask was charged with the raw product, as obtained from the above-described reaction, 100 g of dry ether and 43.6 g (0.44 mol) of NMP. The flask was further equipped with an addition funnel, nitrogen inlet, a cooler and a magnetic stirrer. 20.3 g (0.44 mol) of ethanol was diluted with 25 g of dry ether and added dropwise to the solution. Halfway through the addition of the ethanol, the reaction mixture was heated to 40°C. After the addition was complete, the reaction was allowed to proceed for 2 h at 40°C. Thereafter, the NMP-salts were removed using a 0.2 μm filter. The salts were thoroughly rinsed with dry ether to recover as much of the product as possible. The filtrate was put into the freezer for 1 night and the residual precipitated salts were filtered off through a 0.2 μm filter. The ether was removed with a rotation evaporator, yielding 29.7 g (45%) of raw bis(dimethylethoxysilyl)norbornane. The product was further purified by spinning band distillation (T_b = 85°C, p = 0.1 mbar).

^{1}H-NMR ($CDCl_3$); δ (ppm): 0.05 (dd, Si-CH_3), 1.15 (m, Si(O$CH_2\underline{CH_3}$)$_2$), 3.61 (dq, Si(O$\underline{CH_2}CH_3$)$_2$), 0.52 - 0.77 (m, Si-CH, norbornane), 0.90 - 2.40 (m, C_5H_8 - norbornane).

^{29}Si-NMR ($CDCl_3$); δ (ppm): -50 – -53 (m).

Synthesis and crosslinking of the prepolymers

For the synthesis and the crosslinking of the prepolymers, similar procedures have been followed as have been described in a publication and in chapter 3 of this thesis.[6,7] The only difference was a small adjustment during the working-up procedure. The two prepolymers based on BENOR and BNOR were almost insoluble in methanol, but the main part of both prepolymers was soluble in hexane. The cured polymers were prepared from the particular prepolymers of the hexane fractions.

Characterization

^{1}H-NMR spectra were taken with a Varian Gemini-200 spectrometer (199.97 MHz) in $CDCl_3$ and using $CHCl_3$ as an internal standard. Tetramethylsilane (TMS) was used as the external standard (0 ppm). ^{29}Si-NMR spectra were recorded on a Varian VXR300 with TMS as the external standard (0 ppm).

Thermogravimetric Analysis (TGA) was performed on a Perkin-Elmer TGA-7 apparatus operating at a scanning speed of 10^{o}C/min and in a nitrogen atmosphere. For the measurement a ceramic pan was used. The conventionally used platinum pans are solubilized by the polymer due to a strong complexation of platinum with (residual) silicon-vinyl groups of the polymer. Glass transition temperatures of the prepolymers were determined using a Perkin-Elmer DSC-7 apparatus and the rate of heating was 10^{o}C/min. For the crosslinked polymers, DSC measurements were performed on a TA-Instruments MDSC 2920 (Modulated Differential Scanning Calorimetry) apparatus. For the MDSC measurements, the average sample weight and the overall scan speed were 12 mg and 3^{o}C/min, respectively. The amplitude was 1.0^{o}C with a period of 60 s in all measurements. The glass transition temperature was defined as the midpoint of the DSC-curve. Tensile strength measurements were performed on a Instron 4301 tensile tester at conditioned room temperature (20^{o}C). The crosshead speed was 10 mm/min with a gauge length of 25 mm.

RESULTS AND DISCUSSION

Synthesis of the monomers

The chemical structures of the three synthesized alkoxysilanenorbornane derivatives, and the corresponding synthesis routes are shown in Figure 1.

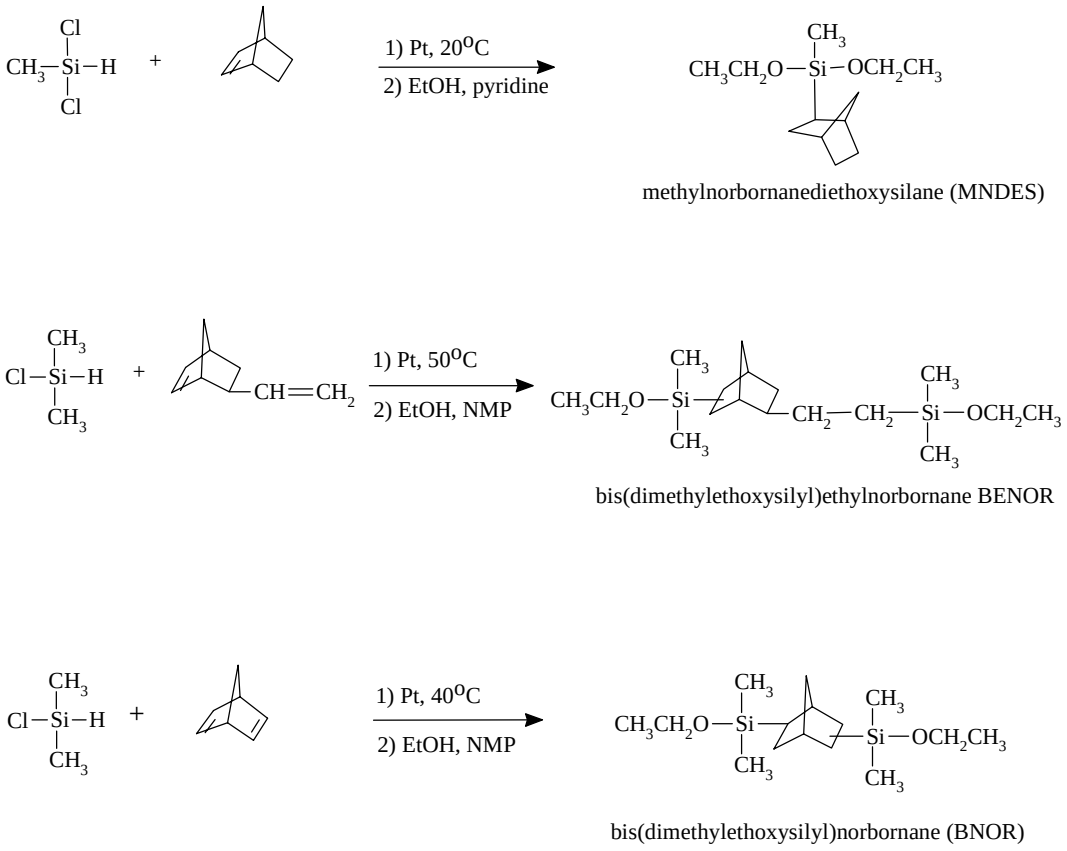


Figure 1. *Reaction schemes for the synthesis of norbornane alkoxysilane derivatives.*

The synthesis of these nonbornane-containing siloxy-monomers only succeeds if chlorosilanes are used as the starting silane.[3,8] Alkoxysilanes were found not to be reactive enough for the hydrosilylation coupling reaction with norbornylene or norbornadiene. The chloro-atom directly connected to the silicon is rather

electronegative, making the hydro-atom more reactive and susceptible to an addition with double bonds. Because the double bonds of unsaturated norbornanes are not that reactive, the addition of chlorosilanes resulted in low yields and fairly long reaction times, still (Table 1).

Table 1. *Conversion times and yields of the syntheses of norbornane alkoxysilanes.*

monomer*	hydrosil. reaction time (days)	temperature (^{o}C)	Yield (%)
MNDES	1	20	23**
BENOR	4	50	29**
BNOR	14	40	45***

* *The abbreviations are according to the name given to the final alkoxysilane products.*

** Y*ield after distillation.*

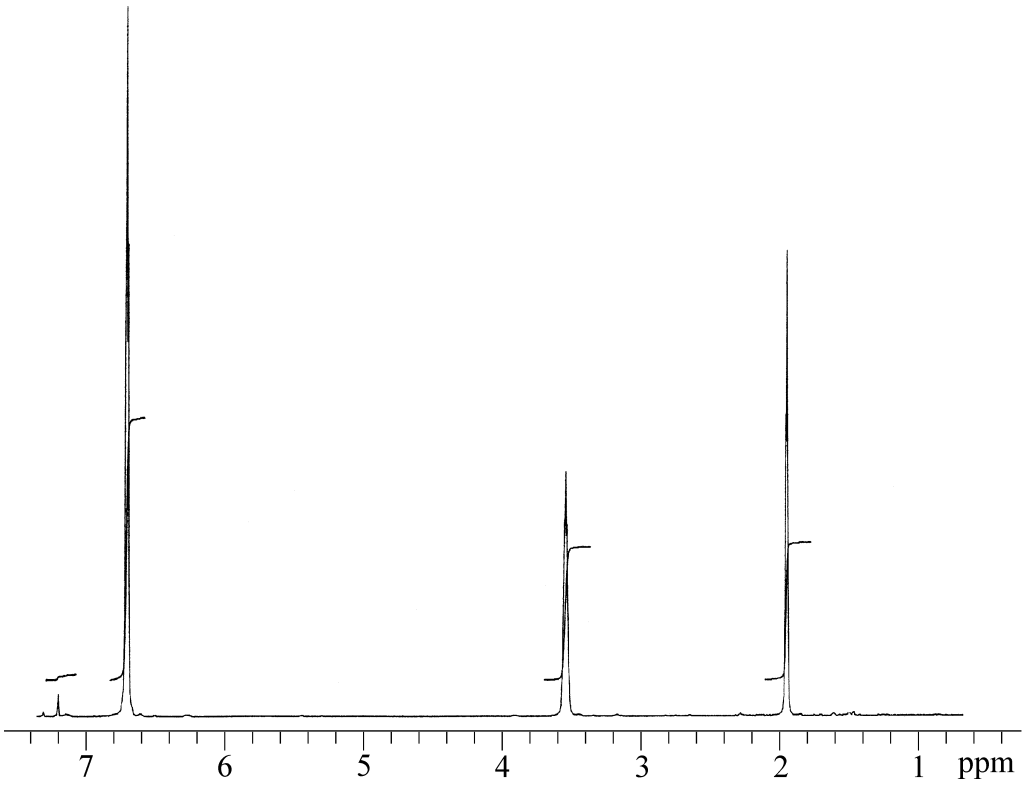
*** *Yield before the distillation procedure.*

Addition of methyldichlorosilane to norbornylene went fairly fast in about 24 hours and in a reasonable yield. Because of the high reactivity of the chlorosilanes with, for instance, water, the reaction mixtures were used impurified for the alkoxylation reaction.

In the derivatization of norbornadiene, a difference in reactivity of the two double bonds is found, as soon as one of the two double bonds reacts. Initially, there is no difference. Both double bonds have exactly the same position in the ^{1}H-NMR-spectrum (6.75 ppm), meaning that the electron densities are the same. When one of the bonds reacts, the other double bond shifts dramatically to 5.95 - 6.15 ppm, indicating a lower local electron density and, therefore, a lower reactivity towards hydrosilylation. Indeed, we observed that the double bond resonating at high field in the NMR needs long reaction times for a reasonable conversion. The way the reaction evolves has been monitored with ^{1}H-NMR. The corresponding NMR spectra are presented in figure 2. Figure 2a shows the spectrum of the pure norbornadiene which has simple peak characteristics. Figure 2b shows the spectrum for the reaction mixture after two hours. The NMR spectrum of the reaction mixture after 1 day is shown in

figure 2c. The reaction with one of the two initial double bonds was complete and a complex spectrum for the norbornane fragment resulted. Figure 2d presents the spectrum for the alkoxylated product after purification. The complex peak structure at the silicon-methyl position is attributed to *endo* and *exo* addition, and to the position of the two silane groups relative to each other (stereochemistry).[3,4,5] A more or less similar difference in reactivity has been found for vinyl-norbornene. Here, the pendant vinyl group was found to be more reactive towards the hydrosilylation reaction, although its peak position in the NMR was 4.8 - 5.5 ppm, whereas the double bond in the norbornene ring structure was resonating at around 6.0 ppm. The higher reactivity of the pendant vinyl group is ascribed to a better accessibility due to less steric hindrance.

2a



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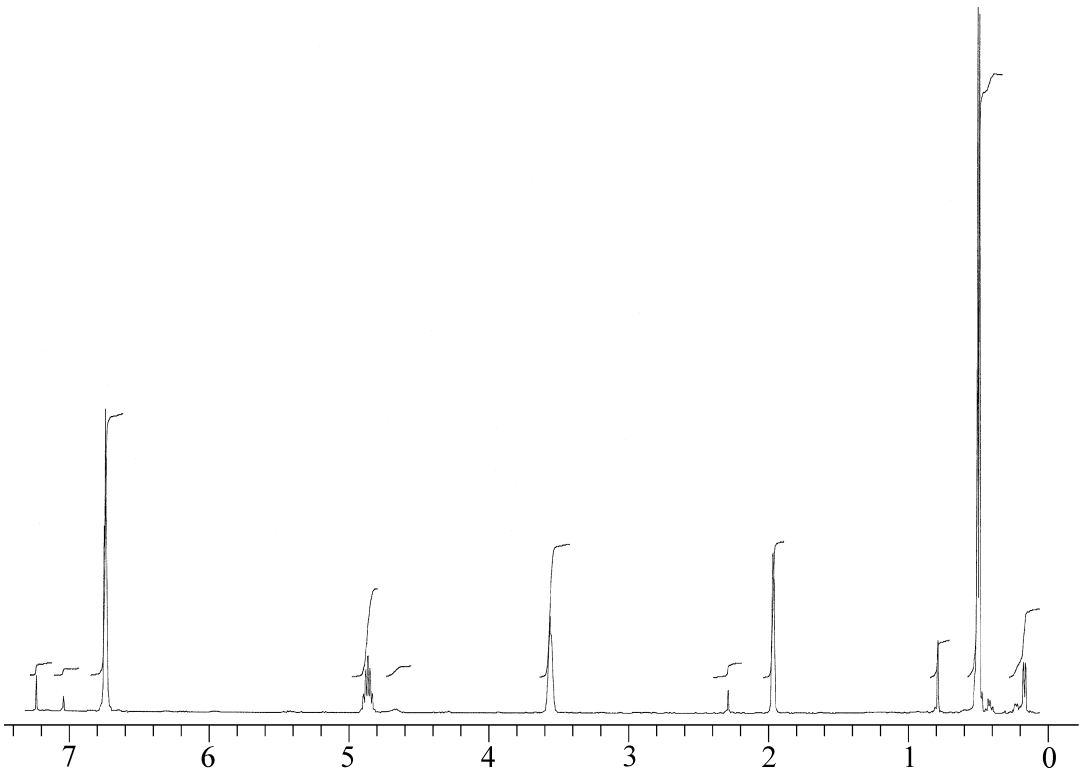

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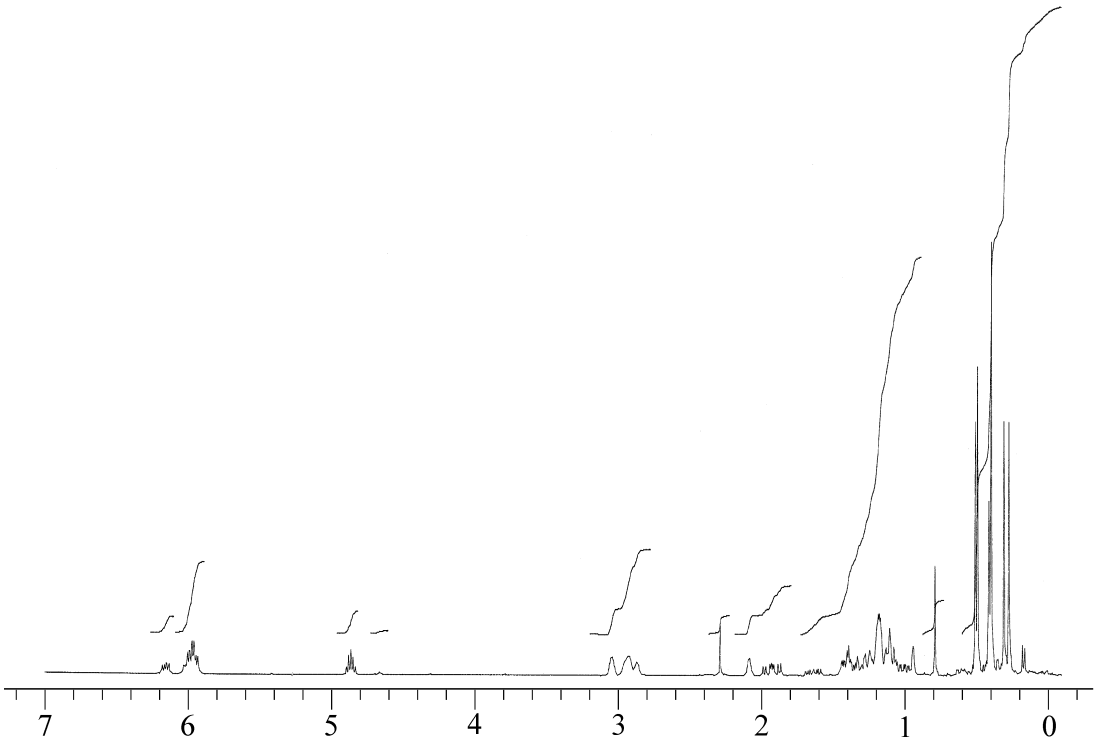

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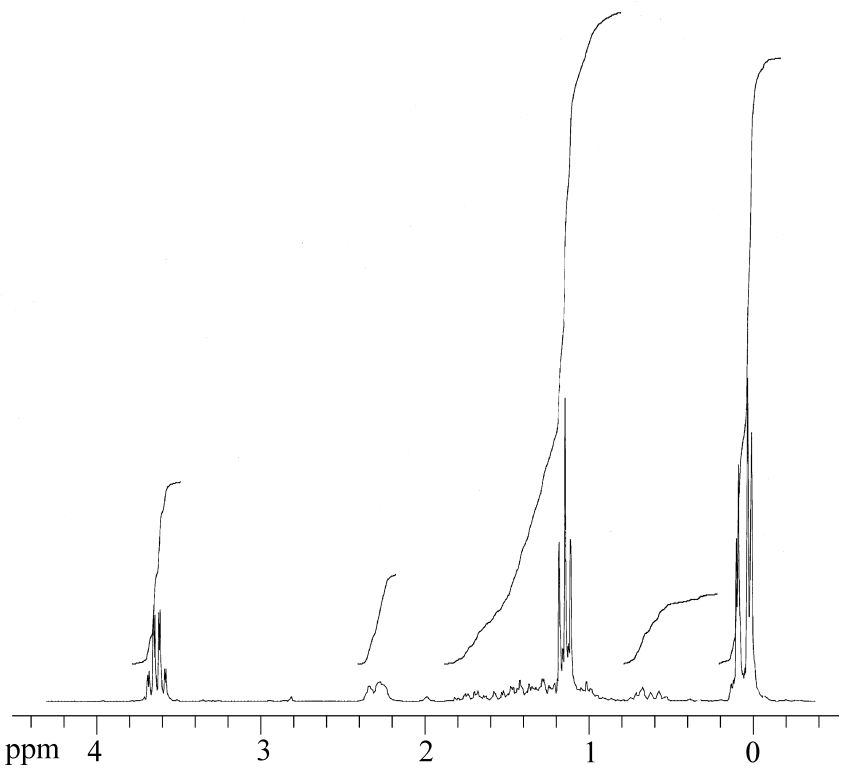

Figure 2. *The relevant ^{1}H-NMR spectra of the pure compounds and of the reaction mixture for the synthesis of bis(dimethylethoxysilyl)norbornane (BNOR). 2a: pure norbornadiene, 2b: the reaction mixture after two hours, 2c: the reaction mixture after1 day and 2d: the purified alkoxylated product.*

Synthesis of prepolymers

The norbornane-derived alkoxysilane monomers were polymerized successfully to polysiloxane prepolymers by the method of cohydrolysis and condensation. Table 2 shows the starting ratios in the monomer feed and the compositions of the prepolymers as determined with ^{1}H-NMR.

In all three cases, the non-functional chain-extending monomer dimethyldiethoxysilane (DMDES) was fully or partly replaced by the norbornane-derived monomer. Similar synthesis and working-up procedures were chosen as have been used for the previously described phenylmethylvinylhydro-siloxane prepolymers.[6,7]

Table 2. *Chemical compositions of the prepolymers expressed in mol fractions.*

monomer	polymer composition based on starting monomer feed
MNDES	poly(phenyl$_{(0.30)}$MNDES$_{(0.30)}$vinyl$_{(0.20)}$hydro$_{(0.20)}$)siloxane
BENOR	poly(phenyl$_{(0.30)}$methyl$_{(0.20)}$BENOR$_{(0.10)}$vinyl$_{(0.20)}$hydro$_{(0.20)}$)siloxane
BNOR	poly(phenyl$_{(0.30)}$methyl$_{(0.20)}$BNOR$_{(0.10)}$vinyl$_{(0.20)}$hydro$_{(0.20)}$)siloxane

monomer	polymer composition found
MNDES	poly(phenyl$_{(0.28)}$MNDES$_{(0.31)}$vinyl$_{(0.22)}$hydro$_{0.19)}$)siloxane
BENOR	poly(phenyl$_{(0.28)}$methyl$_{(0.29)}$BENOR$_{(0.08)}$vinyl$_{(0.20)}$hydro$_{(0.15)}$)siloxane
BNOR	poly(phenyl$_{(0.25)}$methyl$_{(0.29}$)BNOR$_{(0.09)}$vinyl$_{(0.23)}$hydro$_{(0.14)}$)siloxane

All three monomers were completely soluble in the monomer mixtures, which is very important for a homogeneous polymerization. During the polymerizations no changes in polymerization kinetics or behavior have been observed. The norbornyl groups do not introduce important changes in the electronic environment of the silicon atom and by that do not influence the reactivity of the alkoxy groups to any noticeable extent. ^{1}H-NMR-spectra of the MNDES monomer and the prepolymer based thereon are shown in Figure 3. A part of the molecular structure is visualized in Figure 4.

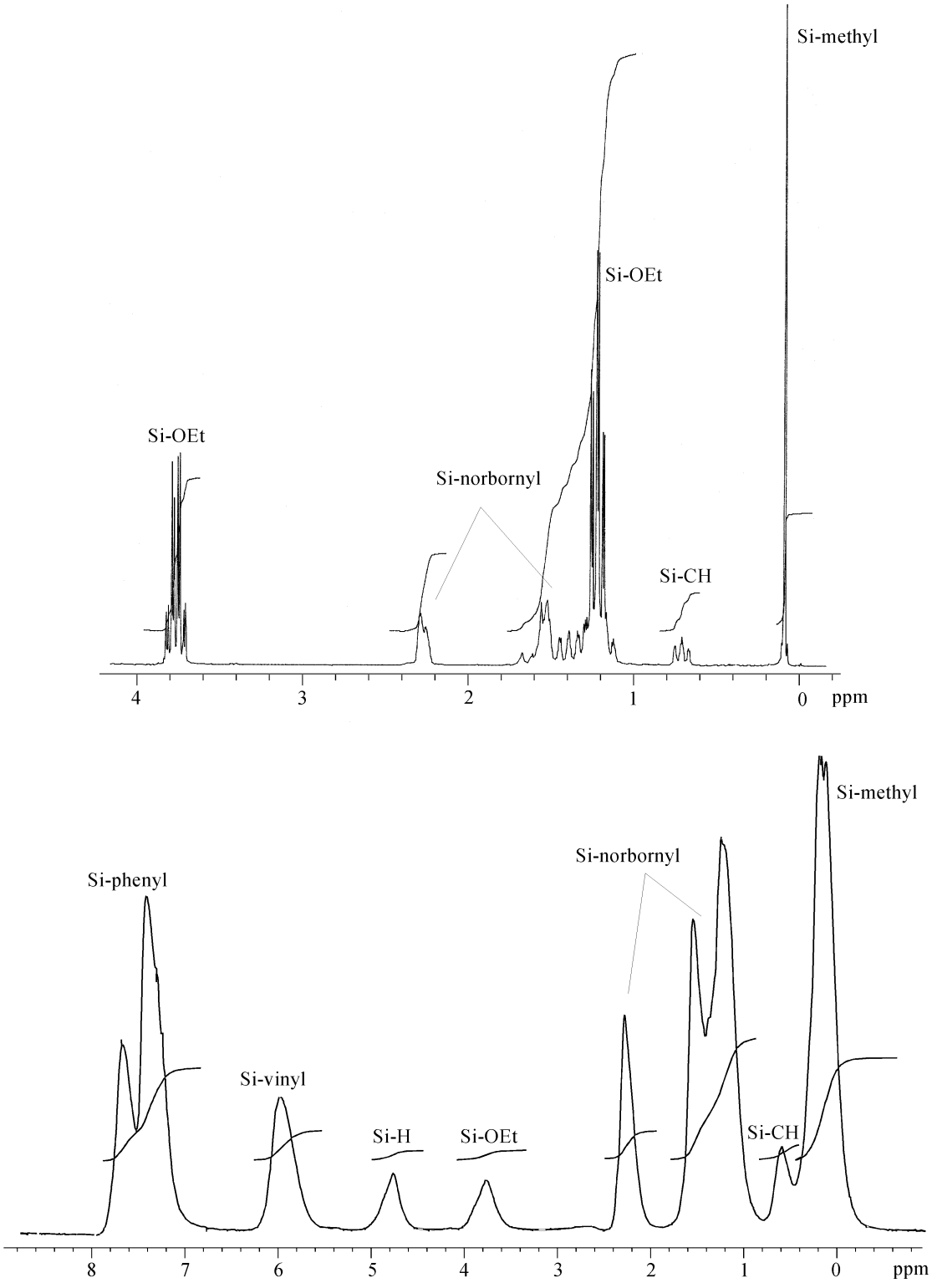

Figure 3. *The ^{1}H-NMR spectra of methylnorbornanediethoxysilane and of a siloxane prepolymer prepared therefrom.*

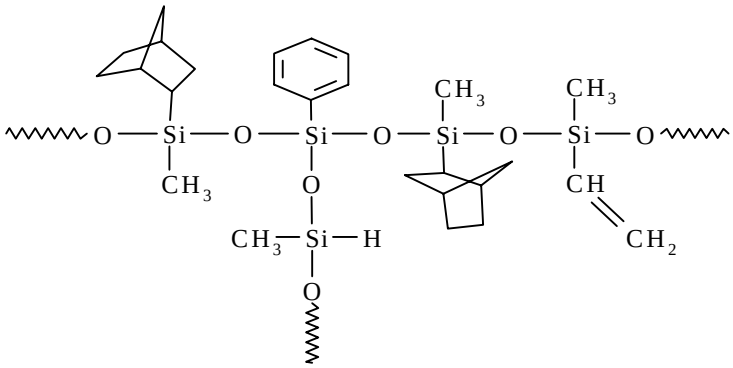

Figure 4. *A part of the molecular structure of the branched prepolymer based on methyl-norbornanediethoxysilane (MNDES).*

Figures 5 and 6 show a part of the molecular structure of the BENOR- and BNOR-based prepolymers, respectively.

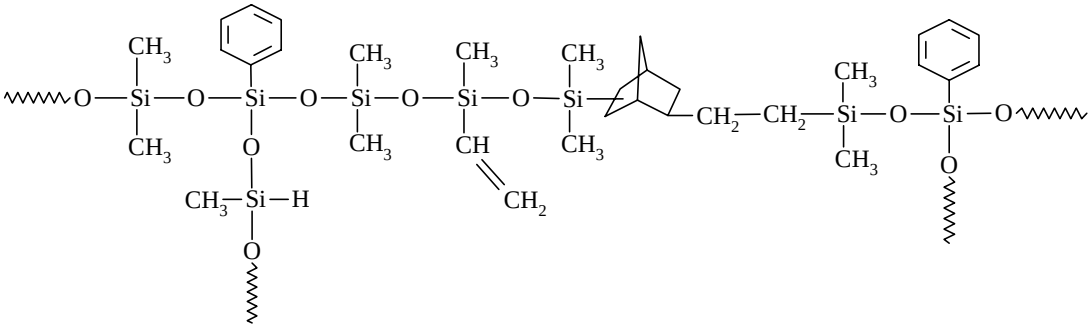

Figure 5. *A part of the molecular structure of the branched prepolymer based on bis(dimethylethoxysilyl)-ethylnorbornane (BENOR).*

During the working-up procedure of the BENOR- and the BNOR-based prepolymers, it has been found that the prepolymers obtained were poorly soluble in methanol. This is attributed to a change to a more apolar molecular structure as compared to prepolymers based on methylnorbornanediethoxysilane and dimethyldiethoxysilane.

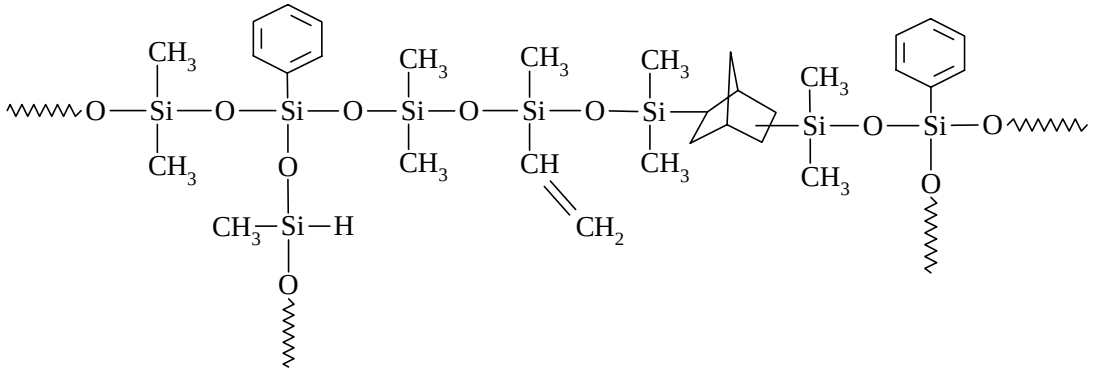

Figure 6. *A part of the molecular structure of the branched prepolymer based on bis(dimethylethoxysilyl)norbornane (BNOR).*

Properties of the cured polymers

Vulcanization of the prepolymers takes place by intermolecular crosslinking through hydrosilylation. This requires only a very low amount of platinum catalyst (1 ppm). To reach maximum conversion with such a low amount of catalyst, long curing times are necessary (~ 24 hours).

The glass transition temperature of the MNDES-based network measured with MDSC was found to be 115^{o}C, which is 85^{o}C higher than found for the DMDES-based network (Table 3). The bulkiness of the norbornyl substituent effectively restricts mobility around the flexible siloxane bonds, resulting in a high-T_g polymer network.

From a measurement of the mechanical properties, a tensile strength of 36 MPa was found (Table 5). This value is significantly higher than the value found for the comparable dimethyldiethoxysilane-based polymer, which had a tensile strength of 23 MPa and a T_g of 41.5^{o}C.[1,2] Because the T_g is now far above room temperature, a hard and glassy material is obtained. This feature gives the material a brittle character comparable to, for instance, poly(styrene). As commonly found for glassy brittle

polymers, a high value for the E-modulus of 1340 MPa and a low strain at break (4.5%) were measured. At temperatures close to its T_g, the material will become tougher in analogy to the dimethyldiethoxysilane-based polymer networks.[1,2] This extends the mechanical reliability of this system to higher temperatures. The course of the stress versus the strain is shown in Figure 7. In the same figure the stress-strain curves of the BENOR- and BNOR-networks are presented.

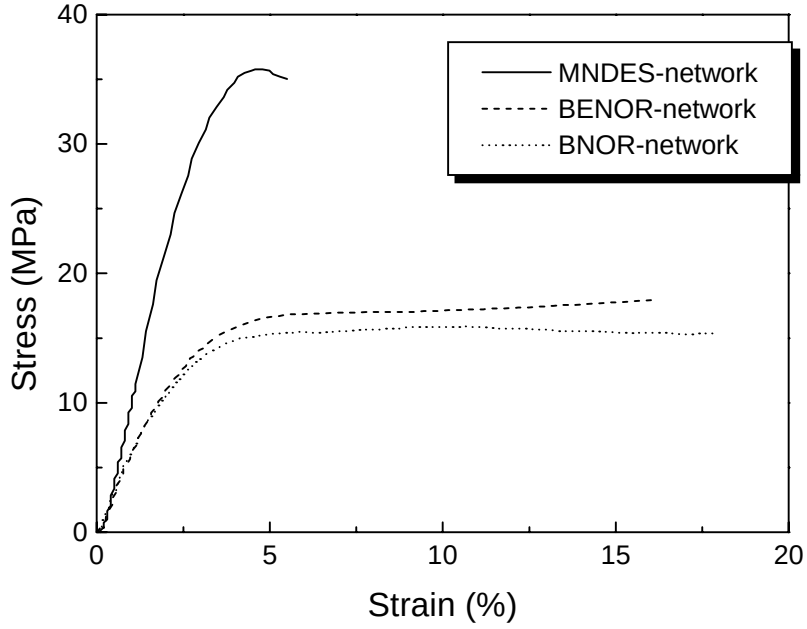

Figure 7. *Stress-strain behavior of the norbornane-derivatized polycarbosiloxane networks at 20°C. The values of T_g are 115, 43 and 33°C for the methylnorbornanediethoxysilane (MNDES)-, the bis(dimethylethoxysilyl)ethylnorbornane (BENOR)- and the bis(dimethylethoxysilyl)norbornane (BNOR)-based networks, respectively.*

The glass transition temperature of the BENOR-based polymer network was found to be 43°C, which is about 13°C higher than that found for the DMDES-based polymer with the same mol fraction of PTES (the vinyl and hydrido contents in the monomer feed were held constant). Incorporation of a rigid group into the backbone effectively

alters the segmental mobility of these systems. One might expect a larger increase of T_g to result from the incorporation of the very bulky norbornane groups into the chemical backbone, however. As we have seen before, the segmental mobility of a crosslinked material is an interplay between the effective crosslink density and the flexibility of the backbone groups and the side groups. In densely crosslinked polycarbosiloxane networks, the crosslink density has been shown to have the largest effect on the final value of the T_g.[1,2] A reason for a lower crosslink density may be that the BENOR and BNOR monomers, because of their length, act as a sort of chain extenders in comparison with DMDES. Moreover, due to the ethenyl unit connected to the norbornane fragment of the BENOR monomer, the chain mobility increases again. For the BNOR-derivatized polycarbosiloxane network a value of T_g of 33^{o}C was found. This is 10^{o}C lower than the value found for the BENOR-network. An important reason is the lower amount of PTES in its backbone structure (about 3 mol % less). This gives rise to fewer bulky groups and a lower crosslink density. One would expect a more efficient increase of T_g for the BNOR polymer than for the BENOR polymer. From the T_gs of the crosslinked polymers, normalized to the mol % of built in monomer, one can indeed derive a more efficient increase of the glass transition temperature of 2.1^{o}C/mol % BNOR against 1.6^{o}C/mol % BENOR. The same feature is observed for the T_gs of the prepolymers (Table 4). Moreover, for the prepolymers the incorporation of norbornane groups into the backbone gives a stronger increase in T_g per mol % groups than their introduction as side group. However, after crosslinking, the opposite is found. As mentioned above, this may be due to a lower effective crosslink density. Another explanation may be that in a tight network configuration the bulky side groups are more effective in reducing chain mobility. The effective crosslink densities of these networks have not been determined.

Table 3. *The glass transition temperatures of the dimethyldiethoxysilane (DMDES)- and norbornane-based polycarbosiloxane networks. The effective increase of the T_g relative to the DMDES based polymers (ΔT) is given as well.*

Norbornane monomer	T_g DMDES* polymer (^oC)	T_g norbornane Polymer (^oC)	ΔT (^oC)	ΔT (^oC/mol %)
MNDES (31 mol %)	30	115	85	2.7
BENOR (8 mol %)	30	43	13	1.6
BNOR (9 mol %)	14	33	19	2.1

***** This column presents the T_g values for the DMDES analogue polymers (DMDES instead of norbornane groups).

Table 4. *The glass transition temperatures of the DMDES- and norbornane-based polysiloxane prepolymers and the effective increase of the T_g relative to the DMDES- based prepolymers.*

Norbornane monomer	T_g DMDES* prepolymer (^oC)	T_g Norbornane prepolymer (^oC)	ΔT (^oC)	ΔT (^oC/mol %)
MNDES (27 mol%)**	-57	-43	14	0.5
BENOR (8 mol%)	-78	-66	12	1.5
BNOR (9 mol%)	-85	-70	15	1.7

* This column presents the T_g values for the DMDES prepolymer analogues (DMDES instead of norbornane groups).

** For the T_g-measurement of the MNDES-based prepolymer, another prepolymer has been used, by exception. This explains the difference in MNDES content in comparison to the polymer reported in table 3 and throughout the text.

Table 5. *The mechanical properties and glass transition temperatures of the norbornane-derivatized polycarbosiloxane networks. The values for the mechanical properties are averages over 4 specimens.*

Polymer	σ_{max} (MPa)	ε_b (%)	E_{mod} (MPa)	toughness (MPa)	T_g (^oC)
MNDES	35.6	4.5	1340	1.1	115
BENOR	19.2	14.2	640	2.2	43
BNOR	16.1	16.1	635	2.2	33

The stress-strain behavior of the BENOR-network is very similar to that of the polycarbosiloxanes described earlier.[1,2] For these networks the mechanical properties are strongly dependent on the value of T_g and, of course, the temperature at which the test is conducted. As the value of T_g of the BENOR-network is 43^{o}C, the stress-strain curve follows a similar course as that for polycarbosiloxane networks based on poly(phenylmethylvinylhydro)siloxanes with the T_g's of 39 - 43^{o}C. A poly(phenylmethylvinylhydro)siloxane network with 30 mol % PTES incorporated, the same amount as contained in the BENOR polymer, has T_g of 39.2^{o}C and a very similar behavior. The monomer PTES is responsible for the branching of the prepolymer and hence for the crosslink density of the network prepared thereof. The crosslink density is an important factor determining the mechanical behavior. The same is valid for the BNOR-network. As the value of its T_g is 10^{o}C lower, and hence quit close to the test temperature of 20^{o}C, the material shows a somewhat more rubbery behavior, which is expressed in a higher average strain.

For these densely crosslinked polycarbosiloxanes, very high thermal stabilities have been found, as is demonstrated by the TGA thermographs in Figure 8. The three systems are almost similar in thermal stability with only some very slight differences in their thermal degradation behavior in the region above 300^{o}C and in residue at 900^{o}C. The BENOR-network has 5 wt% less residue as compared to the BNOR-network, which is attributed to the higher content of carbon in the backbone due to the ethenyl

units. The thermal stabilities are comparable to those of dimethyldiethoxysilane-based polycarbosiloxane networks.[2]

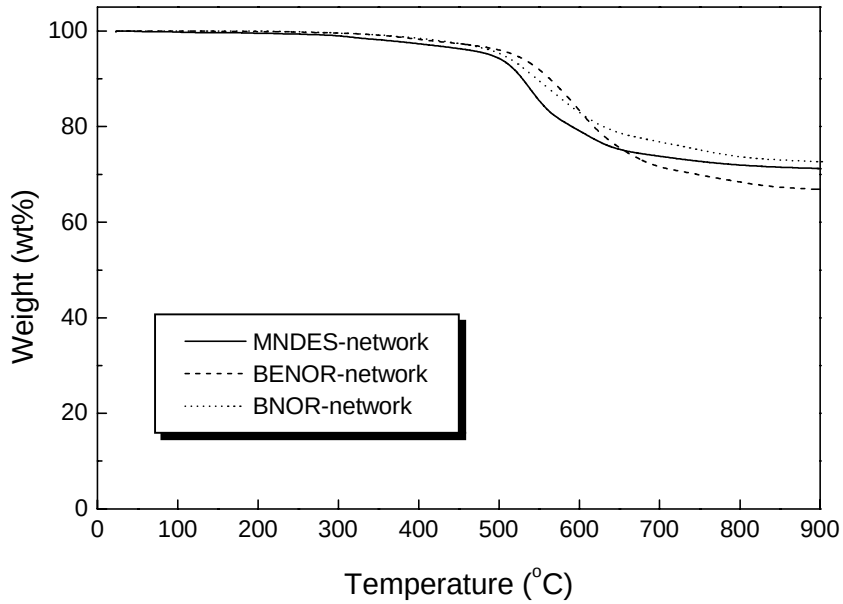

Figure 8. *TGA curves of the norbornane-derivatized polycarbosiloxanes.*

From optical point of view, the new norbornane-derivatized prepolymers are highly transparent. The norbornane groups do not contain UV-absorbing bonds, and thus do not contribute to light-absorbing processes. However, the cured polymers suffer from a severe yellowing effect that occurs during the crosslinking process. Apparently, this is caused by a degradation reaction. Curing at lower temperatures proved to cause much less discoloring. This led to a decrease of the mechanical properties due to a reduced efficiency of the crosslinking reaction, however.

CONCLUSIONS

New norbornane-derived alkoxysilane monomers were synthesized by hydrosilylation addition reactions of chlorosilanes with unsaturated norbornanes followed by alcoholysis. From these new alkoxysilanes, branched self-crosslinkable prepolymers were synthesized, successfully. The norbornane substituents were chosen for their bulkiness combined with their transparency in the UV-visible spectrum, which will allow them to be used in the fabrication of polymer optical fibers with high T_g, good mechanical reliabilty, high temperature stability and high transparency in the visible region.

An effective increase of the T_g has been achieved by incorporation of norbornane-derivatized silanes. The introduction of norbornane as a silicon side group yielded the most effective increase in T_g after the crosslinking reaction. An increase of 85^{o}C was found relative to a similar polymer with dimethylsilane instead of methylnorbornanesilane groups. The material showed high tensile stength and modulus. At room temperature, the material was rather brittle, however. These properties will improve at temperatures closer to T_g (115^{o}C) in analogy to the polycarbosiloxane networks based on dimethyldiethoxysilane. For the (non-crosslinked) prepolymers, the incorporation of norbornane structures into the siloxane backbone showed a more effective increase in T_g than the introduction of norbornane side groups. This result is opposite to that found for the crosslinked polymers.

All three cured polymers showed extremely high thermal stabilities with high residues at 900^{o}C.

The fact that strong yellowing occurred upon curing, which could not be explained, strongly discouraged from doing further research in this direction.

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